

DILUTE SULPHURIC ACID AS A FUNGICIDE.

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Sulphur has been used as a disinfectant, or deodorant, since very ancient times. In The Odyssey reference is made to the burning of sulphur for this purpose. As a parasiticide, insecticide and fungicide it is extensively used at the present time.

The value of sulphur as a fungicide in destroying epiphytic fungi, particularly the powdery mildews of the rose, vine, hop, etc., is well known. Sulphur is also sometimes used in destroying the spores of endophytic fungi, or at least in preventing their growth. As a fungicide sulphur is used or applied in several ways. (1) In the sublimed form (flowers of sulphur) it is dusted on the plants. (2) Both sublimed sulphur and ground roll-sulphur, or "brimstone" (flour of sulphur), are mixed with water to form a paste, which is applied to the heating pipes in green-houses, the finely divided vaporized sulphur thus produced collecting on the plants; or small pieces of roll-sulphur may be carefully heated on a sand bath, the finely divided vaporized sulphur being distributed in the same way; or sulphur in the form of an impalpable powder known as "ventilated sulphur" may be used, as in Germany and Italy where it is used for fighting the vine blight. (3) Sulphur is also applied in combination with lime in the form of solution, as in the "lime-sulphur" washes, these being solutions of a number of sulphides and lower sulphates of calcium.

Sulphur is insoluble in water and is not affected by most reagents under ordinary conditions, and of itself could not be considered to have fungicidal properties. Nor is it likely that it exerts a mechanical action like certain of the insecticides, as pyrethrum flowers, or insect powder, which act by closing the breathing pores of the insects. The action of sulphur as a fungicide is probably due, then, to certain compounds of sulphur which result from the manner of

using it. It is generally considered by plant pathologists that when sulphur is used in a powdered form as a remedy for plant diseases, the effects are due to sulphur dioxide. While sulphur dioxide undoubtedly does have a powerful fungicidal action, it is usually conceded that sulphur dioxide and sulphurous acid are exceedingly toxic to higher plants as well. Owing to the high temperature at which sulphur inflames (260° C.) and the rapid evolution of sulphur dioxide, as well as its unequal diffusion, sulphur is never burned in order to secure its fungicidal effects, but is employed either in the form of a powder, or by gently heating it, when a certain portion of it is sublimed, thus distributing it over the plants in a finely divided state. In Italy the grape-growers and horticulturists have found that the efficiency of powdered sulphur when dusted on plants is in direct ratio to the degree of fineness.

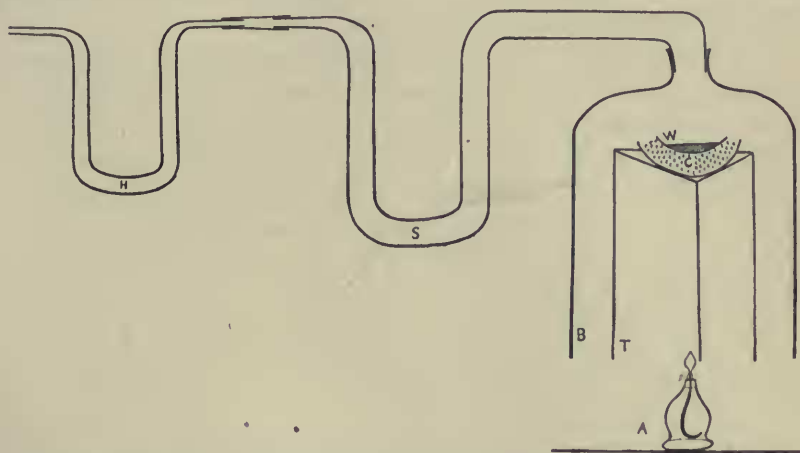
It is stated by Bloxam¹ that "finely divided sulphur, especially sublimed sulphur, is gradually oxidized and converted into sulphuric acid when exposed to moist air." It is also well known that sublimed sulphur contains a certain amount of sulphuric acid. Not only is this true, but it is claimed that if the sublimed sulphur be not dried after washing it to free it of acid, sulphuric acid is again formed. Furthermore, it has been shown by Pollacci² that, independent of the presence of organic matter, sulphur is changed directly into sulphuric acid when mixed with the soil.

The fact that sulphur is easily oxidized in a moist atmosphere to sulphuric acid taken together with the fact that sulphur when vaporized on steam pipes is more efficient as a fungicide than when the flowers, or flour, of sulphur are dusted on the plants, led to the supposition that this increased efficiency might be due to the increased proportion of sulphuric acid formed. Accordingly, experiments were undertaken to determine what compounds are formed when sulphur is slowly heated. An apparatus was constructed for heating sulphur and for collecting the gases formed. The apparatus for collecting the gases consists of a bell jar connected with two U-tubes. The bell jar is suspended over a plate in such a manner as to permit of the free entrance of air from below, or at a distance of 5 to 10 cm.

¹ Bloxam's Chemistry, seventh edition, 1890, p. 189.

² Pollacci, *Gaz. chim. ital.*, through *Jour. Pharm. Chim.*, 1874, p. 330.

above the plate. The sand bath used for heating the sulphur is placed on a glass tripod under the bell jar, and an alcohol lamp is used to heat the sand. A definite quantity of N/10 sodium carbonate solution is placed in the U-tubes and the free end connected with an aspirator, or suction pump.



Apparatus for heating sulphur and collecting acid gases formed. *A*, alcohol lamp; *T*, glass tripod; *C*, porcelain dish containing sand; *W*, watch crystal containing sulphur; *B*, bell jar supported by a clamp; *S*, U-tube with one end ground to fit bell jar and containing 15 c.c. of tenth normal sodium carbonate solution; *H*, U-tube containing distilled water, and having one end connected with U-tube, *S*, by means of rubber tubing, and the other with an aspirator.

The operation was conducted as follows: To the first U-tube, which was well ground to fit the opening in the bell jar, were added 15 c.c. of tenth normal sodium carbonate solution to combine with the sulphur acids formed. To the second U-tube 5 c.c. of water were added. Definite quantities of sulphur were weighed out in a watch crystal, and heated on the sand bath for several hours. The heat was regulated to a certain extent so as to minimize the loss of the vaporized products due to their escaping from below the bell jar, that is, the flame was removed at times and the space between the plate and bell jar was reduced to but a few centimeters. At the end of the operation the apparatus was allowed to cool, and the watch crystal containing the sulphur weighed to determine the total

loss of sulphur by vaporization. The contents of the two U-tubes were then poured into a graduate and the U-tubes, the bell jar and the plate carefully rinsed with distilled water and the rinsings added to the graduate, the contents of which was made up to about 200 or 300 c.c. One-half the quantity of solution was used for determining the sulphuric acid formed, while the other half was used for determining the sulphurous acid present.

To the portion used for determining the sulphuric acid 5 additional c.c. of tenth normal solution of sodium carbonate were added, and the solution titrated with tenth normal sulphuric acid, using methyl orange as indicator. The difference between the number of c.c. of sodium carbonate solution used and the number of c.c. of sulphuric acid solution consumed gives the equivalent of sulphur acids formed. That the greater proportion of acids formed under the conditions described is sulphuric acid, is shown by adding barium chloride with an excess of hydrochloric acid to a hot solution, the precipitate formed being insoluble. The amount of sulphur converted into sulphuric acid is very easily calculated.

The other half of the original solution was titrated with decinormal iodine solution using starch test solution as indicator, but it was found that the proportion of sulphurous acid formed by heating or subliming the sulphur in the manner indicated was quite small.

In the following table the results of a number of experiments are given:

	Weight of Sulphur Heated.	Number of Hours Heated.	Loss of Sulphur by Vaporization.	Percentage of Vaporized Sulphur Converted Into Sulphuric Acid.	Percentage of Vaporized Sulphur Converted Into Sulphurous Acid.	Percentage of Vaporized Sulphur Driven Off as Sublimed Sulphur.	Remarks.
1	0.200	3	0.050	8.02	0.31	91.67	
2	0.500	3	0.120	7.08	0.53	92.39	
3	0.500	3	0.110	7.57	0.28	92.64	
4	0.500	3	0.120	9.53	0.10	91.37	
5	0.500	3	0.128	8.72	0.24	91.04	
6	0.500	3	0.150	13.64	0.31	86.05	
7	0.500	5	0.200	7.08	0.15	92.77	
8	1.000	7	0.030	25.34	0.26	73.40	Very slowly heated.
9	1.000	8	0.035	28.03	none	71.97	Very slowly heated.
10	2.000	3	0.880	6.90	0.25	92.85	Rapidly heated.
11	1.000	3	0.975	3.76	0.29	95.95	Rapidly heated.
12	3.000	3	1.085	1.68	1.38	96.94	Rapidly heated.

The table shows that when sulphur is heated very slowly with free access of air a large percentage (nearly one-third) of the vaporized sulphur is converted into sulphuric acid, very little or no sulphurous acid being formed. When the temperature is increased and the sulphur more rapidly vaporized, the percentage of sulphuric acid formed is very much smaller, the percentage of sulphurous acid formed remaining about the same. When the sulphur is heated rapidly with access of less air the proportion of sulphurous acid is increased while the percentage of sulphuric acid formed is very much lessened. It is of course difficult to carry on an experiment for collecting the gases formed which would at the same time simulate the conditions in a greenhouse where there is free access of air and the temperature is comparatively low. But the results of my experiments as given in the table would lead to the inference that a large percentage of sulphuric acid would be formed and very little or no sulphurous acid, as shown in experiments 8 and 9.

While it is known that sulphurous acid has marked germicidal properties and while a small percentage of sulphurous acid is produced when sulphur is heated under certain conditions, still owing to the large percentage of sulphuric acid produced when sulphur is heated under conditions which more nearly simulate those where sulphur is heated on steam-pipes in the green-house, the question arose as to whether sulphuric acid has not marked fungicidal action and as to whether it is not one of the active agents when sulphur is used as a fungicide. In order to determine whether sulphuric acid has fungicidal properties a number of experiments were carried out.

SPRAYING EXPERIMENTS.

During the summer of 1904 some preliminary experiments were conducted to determine what strength of solution of sulphuric acid could be used for spraying plants without injurious effects. In this series of experiments the solutions were made with distilled water, and used in strengths varying from 1 part in 200 to 1 part in 10,000. The plants experimented with were the common field plants, such as wild cherry, elder, ailanthus, phytolacca, yellow dock, burdock, abutilon, blackberry, wild rose, milkweed, locust, etc. An ordinary

hand atomizer was used for the spraying operation, and the plants were usually sprayed late in the afternoon so as to avoid concentration of the solutions before they were absorbed, as also the burning effects of the sun. It was found that a solution of 1 to 200 produced a marked burning effect on the leaves, and in the case of some plants, as blackberry, polygonatum, oxalis, pear, rose, mulberry, raspberry, etc., contiguous parts of the plant exhibited signs of injury.

It was soon found that there is considerable difference in the resisting power of plants when sprayed in this manner. The most sensitive plants were peach, raspberry and wild carrot, while the most resistant were poison ivy and plantain (*Plantago major*). As a result of these experiments it was found that most plants could be sprayed with a solution of sulphuric acid varying in strength from 1 part in 500 to 1 part in 1000, without serious injury to the plants, and the conclusion was reached that it would be perfectly safe to use sulphuric acid solution as a spray in the strength of 1 part of acid to 1000 parts of water.

Later in the summer of 1904 it was my good fortune to find a rose garden in which some of the plants were badly affected with mildew and to obtain permission of the rose-grower to treat the affected plants. In the series of experiments a solution having a strength of 1 part of acid to 1000 parts of water was freely applied by means of a garden syringe, so that the plants were thoroughly wetted. Sprayings were made as follows: August 11 at 4 P. M., August 12 at 8 A. M., August 13 at 8 A. M., August 14 at 8 A. M., August 15 at 8 A. M., August 16 at 8 A. M.

Within about a week afterward the mildew had about all disappeared and the young leaves which were putting forth showed no signs of injury. During 1905 the mildew did not re-appear, and it was noticed that the plants which had been sprayed with the sulphuric acid solution the year before had never done better.

It may be of interest to state that parallel experiments using copper sulphate, 1 to 1000, were conducted with the result that while the mildew was eradicated the tips of the young leaves were injured.

During the winter of 1904-05 I had an opportunity of trying the solution on roses growing in the green-house. The plants were

sprayed with solution of sulphuric acid 1 to 1000, on December 7, 8, 9, 10, 12, 14, 16 and 19, with the result that the mildew was completely eradicated, the new growth was vigorous and the mildew did not reappear.

A few months later another lot of roses growing in the greenhouse were treated. These included pink rambler, crimson rambler, Victoria rambler, bridesmaid, golden gate, liberty, American beauty and Carnot. The plants were sprayed with sulphuric acid solution, 1 to 1000, on January 9, 10, 11, 12, 15 and 17, with results similar to those obtained in the previous experiments. I have also used the spray since with similar results.

In conclusion I may add that it appears that dilute solutions of sulphuric acid have a beneficial effect on the plants treated apart from their fungicidal action. In fact they seem to act as a tonic to the host plant while they kill the mildew.

Should subsequent experiments confirm the results here recorded, it will be found that sulphuric acid has certain advantages over sulphur, in that it does not discolor the foliage as sulphur does, its employment is more easily controlled, and it does not have the disagreeable odor of certain other compounds associated with sulphur.

Inasmuch as the antiseptic properties of sulphurous acid are well established, it may be possible that a combination of sulphuric and sulphurous acids in solution would be more effective than sulphuric acid alone. Taking the proportions in which these acids are formed when sulphur is heated, it may be that a solution containing 1 part of sulphuric acid and 0.1 to 0.01 part of sulphurous acid to 1000 parts of water, would be more effective than sulphuric acid alone in the proportion given.